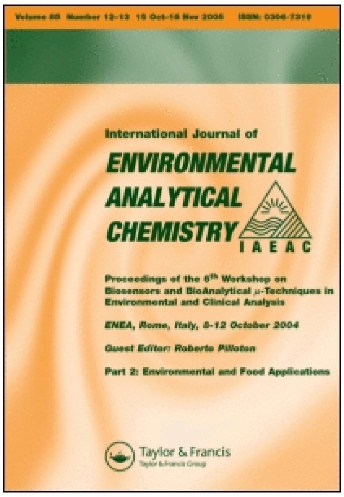

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Junyan Pan[a]; Sui Wang[a]; Ruifeng Zhang[a]
[a] The State Key Laboratory Base of Novel Functional Materials and Preparation Science, Ningbo University, Ningbo, P.R. China

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A novel Pb(II)-imprinted IPN for selective preconcentration of lead from water and sediments

JUNYAN PAN, SUI WANG and RUIFENG ZHANG*

The State Key Laboratory Base of Novel Functional Materials and Preparation Science,
Ningbo University, Ningbo, 315211, P.R. China

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A novel adsorbent Pb(II)-imprinted interpenetrating polymer network (IPN) of epoxy resin-triethylenetetramine and lead methacrylate-acrylamide-1,4-butanedioldiacrylate (BDDA) was synthesized by the metal ionic imprinted polymer (MIIP) technique. The IPN was prepared by *in situ* sequential polymerization, and the coordination interaction of Pb(II) and functional groups of the IPN adsorbent was discussed using FT-IR spectra. The characters of the IPN were investigated by a series of experiments. The experimental results show that trace Pb(II) ions can be quantitatively preconcentrated at pH 4.0 with recoveries $>95\%$. The maximum static adsorption capacity of the ion-imprinted adsorbent was $138.6\,\mathrm{mg\,g^{-1}}$. The imprinted IPN has a higher adsorption capacity and selectivity towards Pb(II). Moreover, the Pb(II)-imprinted IPN shows superior reusability and stability. The precision (R.S.D.) for 11 replicate adsorbent extractions of $20\,\mathrm{ng\,mL^{-1}}$ Pb(II) was 2.9%. The accuracy of the proposed procedure was verified by analysing three standard reference materials. The prepared ion-imprinted IPN adsorbent was applied to three natural samples and also yielded satisfactory results. That is to say, the Pb(II)-imprinted IPN is suitable for environmental Pb(II) ionic selective removal as an SPE adsorbent.

Keywords: Lead; Interpenetrating polymer network; Metal ionic imprinted technique; Selective preconcentration

1. Introduction

Soil and water pollution by toxic heavy metals is a major environmental concern [1]. Among them, lead is the most common environmental pollutant with no biological function, which threatens human life severely [2–4]. Unlike organic compounds, lead is non-biodegradable but accumulates through its association with inorganic and organic matter, e.g. by adsorption processes, formation of complexes, or chemical combinations. Therefore, removal and determination of lead from environment have become the primary aims of current scientific workers [5–7].

Since the first report on lead removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in applications throughout the world [8–10]. But activated carbon is very expensive and requires ligands to improve its removal

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*Corresponding author. Fax: +86 574 87600857. Email: nbzrf@yahoo.com.cn

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performance for heavy metals. Although other adsorbents such as chitosan [11], zeolites [12, 13], clay, and even industrial wastes [14] are widely adopted in applications today, their adsorption capacity and selective removal of lead are still poor. In recent years, metal ionic imprinted technology has become a powerful method for high selectivity adsorption of target metal ions [15–21]. Therefore, in this study, a novel Pb(II)-imprinted interpenetrating polymer network (IPN) of epoxy resin-triethylenetetramine and lead methacrylate-acrylamide-1,4-butanedioldiacrylate (BDDA) was synthesized by the metal ionic imprinted polymer (MIIP) technique. Epoxy resin and triethylenetetramine formed the first network, and lead methacrylate, acrylamide and 1,4-butanedioldiacrylate formed the second network. In our knowledge, Pb(II)-imprinted IPN as SPE sorbent for the preconcentration and determination of Pb(II) has not been employed previously. Comparing with other adsorbents, the imprinted IPN represents a higher adsorption capacity and selectivity towards Pb(II).

2. Experimental

2.1 *Instruments and apparatus*

A Perkin-Elmer AA-6800 atomic absorption spectrometer equipped with Perkin-Elmer single-element hollow cathode lamps and an air–acetylene burner was used for the determination of Pb(II). The instrumental parameters were recommended by the manufacturer. The wavelength selected for the determination of the analyte was as follows: Pb 283.3 nm. A model pHS-3CT digital pH meter (Shanghai Dazhong Analysis Instrument Factory, China) was used to measure pH values. The FT-IR spectra of the Pb(II)-imprinted IPN gel was recorded by Nicolet NEXUS 670 FT-IR spectroscopy (Nicolet Instrument Corporation, Madison, WI). The flow rate of liquid through columns was controlled by a model BT00-100M peristaltic pump (Baoding Laonger Precision Pump, Hebei, P.R. China).

2.2 *Reagents and standards*

Unless otherwise stated, all water used in the experiments was 18 MΩcm distilled deionized water (DDI) purified with a Milli-Q system (Millipore, USA), and all solutions were prepared with DDI water. The standard labware and glassware used were repeatedly cleaned with diluted HNO_3 and rinsed with DDI water according to a published procedure [22].

Epoxy resin, triethylenetetramine, methacrylic acid (MAA), acrylamide and 1,4-butanedioldiacrylate (BDDA), azobisisobutyronitrile (AIBN), and lead nitrate were all purchased from Shanghai Chemistry Regent Limited Company (P.R. China). (http://www.reagent.com.cn/). All reagents used in the experiments were of analytical grade and not purified further. Lead methacrylate was self-prepared by lead nitrate and methacrylic acid, and was dried in a dry box until use. Three different samples were collected from Ningbo region, P.R. China. The river sediment sample was collected from the bank of Fenghua River; the soil sample was collected from the land of Zhenhai; and the surface river sample was collected from Yongjiang River. Three standard reference materials (GBW 07403, soil; GBW 08619, water; GBW 07301, river sediment) were purchased from the National Research Center for GeoAnalysis, P.R. China. (http://nrcga.cags.ac.cn/).

2.3 *Preparation of Pb(II)-imprinted IPN gel*

The Pb(II)-imprinted IPN was prepared by an ion-imprinted technique. Nine grams of epoxy resin and 3 g of triethylenetetramine were dissolved in 10 mL methanol and agitated for about 20 min at 50°C until the viscidity of the mixture began to increase. Three grams of lead methacrylate, 2.0 g of acrylamide, 0.5 g of 1,4-butanedioldiacrylate, and 50 mg of AIBN dissolved in 10 mL of methanol were added into the above mixture. After complete agitation, the mixture system was held still for 6 h at 35°C until the first polymer network of epoxy resin-triethylenetetramine adequately formed by the gelatinizing reaction. Sequentially, the gelatinized mixture was kept at 60°C for 24 h, and the second polymer network of lead methacrylate-acrylamide-1,4-butanedioldiacrylate (BDDA) formed by the copolymerizing and cross-linking reaction. The solid product was ground and screened (40–75 µm size selected for experimental sorbents). The selected particles were treated with $0.5\,\mathrm{mol\,L^{-1}}$ of HNO_3 for 24 h to remove all of Pb(II) in the imprinted IPN, then cleaned by DDI water until neutral equilibrium and dried in a vacuum oven at 65°C for 48 h.

2.4 *Analysis of FT-IR spectra*

The existence of the functional groups in Pb(II)-imprinted IPN was verified and analysed by the FT-IR spectrum. Figure 1 shows that the FT-IR spectra of Pb(II)-imprinted IPN removed Pb(II) (curve *a*) and that of Pb(II)-imprinted IPN saturated with lead ions (curve *b*). According to a previous publication [23], the main absorption peaks can be assigned as follows: $3351.72\,\mathrm{cm^{-1}}$ (curve *a*) and $3386.64\,\mathrm{cm^{-1}}$ (curve *b*) (γ O–H and N–H), 2963.88 and $2963.14\,\mathrm{cm^{-1}}$ (γ C–H of CH_2 and CH), 1665.06 and $1665.31\,\mathrm{cm^{-1}}$ (γ C=O of acylamide), 1606.68 and $1608.10\,\mathrm{cm^{-1}}$ (γ C=C of Ar), 1508.54 and $1508.81\,\mathrm{cm^{-1}}$ (γ C=C of Ar), 1243.59 and $1243.80\,\mathrm{cm^{-1}}$ (γ_{as} C–O–C of O–Ar; γ, stretching vibration; γ_{as}, antisymmetric stretching vibration; Ar, benzene).

Comparing curve *a* with curve *b*, the absorbance peak at 1551.79 $\mathrm{cm^{-1}}$ (curve *b*) should be ascribed to carboxylate groups because of the coordination of Pb(II) and carboxyl. The absorbance peak of carboxyl in curve *a* shifts and is concealed in the peak $1665.06\,\mathrm{cm^{-1}}$ because of the hydrogen bonding. The characteristic absorption peak at $1725.23\,\mathrm{cm^{-1}}$ (curve *a*) is attributed to γ C=O of carboxyl after elution by acid. Meanwhile, the absorbance band between $3500\,\mathrm{cm^{-1}}$ and $2300\,\mathrm{cm^{-1}}$ in curve *a* is obviously wider than that in curve *b* also because of hydrogen bonding. From the comparison, the varieties of positions and intensities of peaks demonstrate that Pb(II) has been coordinated to the functional groups of Pb(II)-imprinted IPN.

2.5 *General procedure for adsorption–desorption of Pb(II)*

The characters of the IPN were investigated by batch experiments. Pb(II) can be adsorbed by the IPN through the differential identification, and it can also be eluted by acid. The mechanism of adsorption–desorption is shown in scheme 1.

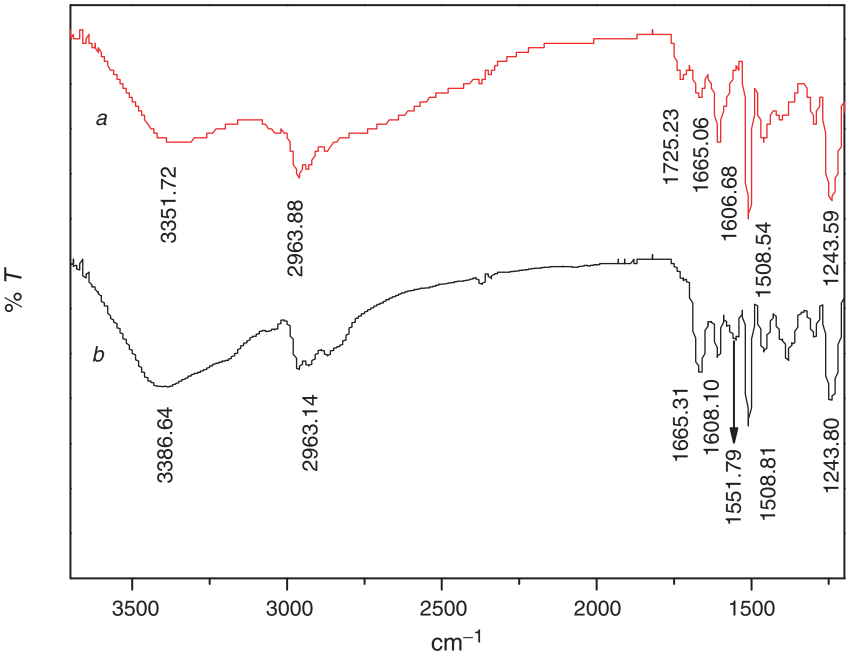
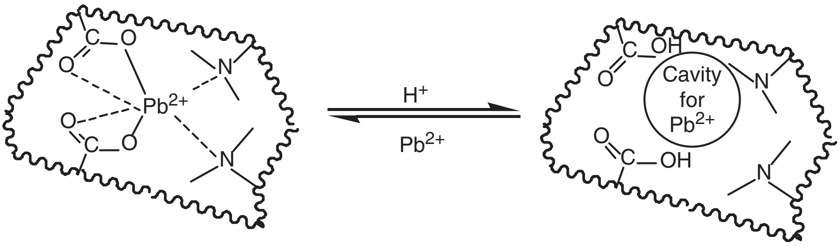


Figure 1. FT-IR spectra: *a* Pb(II)-imprinted IPN having removed Pb(II); *b* Pb(II)-imprinted IPN saturated with Pb(II).



Scheme 1. Adsorption–desorption mechanism of Pb(II)-imprinted IPN.

Moreover, the influence of the medium pH, effects of the initial Pb(II) concentration, adsorption capacity, effect of elution rate, and stability of Pb(II)-imprinted IPN were studied by a series of experiments. The concentrations of the metal ions in the aqueous phases after the desired treatment periods were determined by using a flame atomic absorption spectrometer (FAAS). The instrument response was periodically checked with known Pb(II) solution standards. The adsorbed IPN particles were eluted with 0.5 mol L^{-1} of HNO_3. The solutions passed through the adsorbing columns at a flow rate that could be controlled by peristaltic pump. All experiments were repeated for three times, and the average values were adopted as final results.

2.6 *General procedure of sample treatment*

A portion (10–50 mg) of the river sediment sample was accurately weighed into a 50 mL beaker, and a mixed solution (12 mL of concentrated hydrochloric acid and 4.0 mL of concentrated nitric acid) was added. The beaker was covered with a watch glass, and the mixture was evaporated on a hot plate at 95°C almost to dryness. Then, 8.0 mL of mixed solution was added to the residue. After cooling, the mixture was filtered through a P10 glass filter. The sample was diluted to 10 mL with DDI water and analysed by the general procedure given above. The soil sample was treated by the same procedure for the river sediment sample treatment given above.

The surface river water sample was collected from a dirty part of Yongjiang River (Ningbo, China). The bottle filled with the water sample was cleaned with detergent, DDI water, dilute nitric acid, and DDI water in sequence. The sample was immediately filtered using cellulose filter membranes of 0.45 µm and adjusted to pH 4.0 with the diluted HNO_3 and $NH_3 \cdot H_2O$.

3. Results and discussion

3.1 *Adsorption of Pb(II) on the prepared IPN*

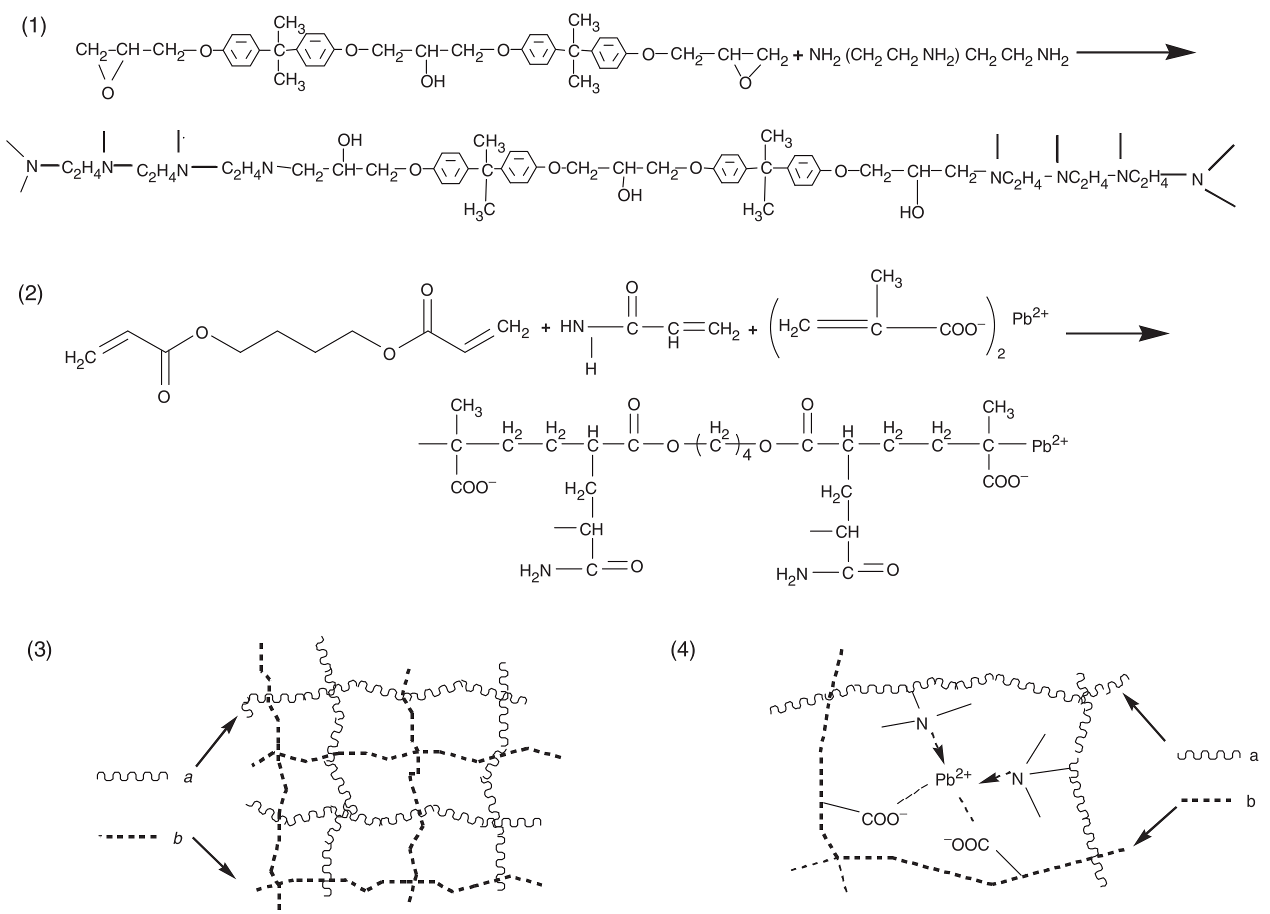
The target polymer was synthesized by the MIIP technique. The selection of MIIP arises from the memory effect of the polymer to the imprinted ions, e.g. from the specificity of interaction of ligands with the metal ions; the coordination geometry and the coordination number of metal ions; and the charge of the metal ions and to a large extent on the size of them [24].

In this study, two sets of polymer networks were adopted in one MIIP system by *in situ* sequential polymerization. The first polymer network was formed by epoxy-resin gelation with triethylenetetramine. The other was formed by lead methacrylate co-polymerization with acrylamide and cross-linker. These interpenetrated each other, forming an interpenetrating polymer network (IPN). Pb(II) as template ion could form lead methacrylate with methacrylic acid, and simultaneously coordinate with amidogen of triethylenetetramine of the first polymer network. So, the cavums were formed by two sets of polymer networks supporting each other (scheme 2). This interpenetrating structure ensures the high recognizing ability to the template ion Pb(II).

3.2 *Influence of solution pH on Pb(II) preconcentration*

For the metal, ionic complexation with ligands is highly dependent on the equilibrium pH of the medium, and the pH value of the solution is an important parameter for adsorbing metal ions. Seven equal concentrations and equal volumes of Pb(II) ion standard solution were prepared and adjusted in the pH range 1–7 with diluted HNO_3 and $NH_3 \cdot H_2O$. Considering hydrolysis of Pb(II) ion in strong alkali solution, no further experiments were carried out when the solution pH was above 7.0.

The results (figure 2) show that the preconcentration of lead was strongly affected by solution pH. The lead preconcentration efficiency was very low at a solution pH



Scheme 2. (1) Gelation reaction of epoxy resin and triethylenetetramine; (2) copolymerization of lead methacrylate, acrylamide and 1,4-butanedioldiacrylate; (3) structure sketch map of the interpenetrating polymer network (IPN); (4) coordination linkage scheme of Pb(II) ion and Pb(II)-imprinted IPN; *a* (wavy line): polymer network of epoxy and triethylene tetramine; *b* (dashed line): polymer network of lead methacrylate, acrylamide and 1,4-butanedioldiacrylate.

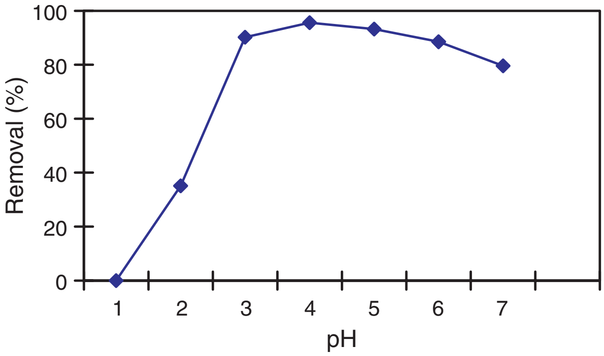


Figure 2. Influence of pH on the preconcentration of Pb(II) on imprinted IPN. Other conditions: 100 mg of Pb(II)-imprinted IPN; 100 mL of 20 μg mL^{-1} of Pb(II).

below 2.0, because of the protonation of IPN. From pH 2.0 to 4.0, the preconcentration efficiency increases sharply with the pH value on the whole. The optimal range of pH value for Pb(II) preconcentration was 4.0–5.0. This is advantageous for lead preconcentration and recovery from wastewater because wastewater is always found to be acidic in order to avoid lead hydrolysis. In this experiment, pH 4.0 was chosen for further experiments.

3.3 *Influence of coexisting ions on Pb(II) preconcentration*

Different foreign ions were added to equal quantities of the diluted standard solutions and adsorbed according to the general procedure. The results showed that up to 4000 μg mL^{-1} of K^{+} and Na^{+}, 200 μg mL^{-1} of Ca^{2+}, Mg^{2+}, Mn^{2+}, and Ni^{2+}, 100 μg mL^{-1} of Cd^{2+}, 50 μg mL^{-1} of Cu^{2+} and Zn^{2+}, and 20 μg mL^{-1} of Hg^{2+} had no significant effect on the determination of 1 μg mL^{-1} of Pb^{2+}. The good selectivity mainly comes from the coordination-geometry selectivity because the Pb(II)-imprinted IPN gel sorbent can provide the ligand groups arranged in a suitable way required for coordination of Pb^{2+}. Moreover, the size of Pb^{2+} exactly fits the cavity of the Pb(II)-imprinted sorbent, thus providing hole-size selectivity. Hence, the Pb(II)-imprinted IPN sorbent exhibits a high selectivity for removal of Pb^{2+} in the presence of other similar transition-metal ions and highly concentrated electrolytes.

3.4 *Adsorption capacity of Pb(II)-imprinted IPN*

Batch experiments were carried out to study the adsorption capacity of the imprinted IPN. A range of concentration solutions of Pb(II) ion were prepared, and the acidity of each solution was adjusted to pH 4.0. A small amount (0.1 g) of the imprinted IPN was added in each of the eight conical flasks. The results show that the amount of lead ions removed per unit mass of the imprinted IPN increased with the initial concentration of the lead ions. In order to reach ‘saturation’, the initial lead ion concentrations were increased until the plateau values were obtained. The results were listed in figure 3.

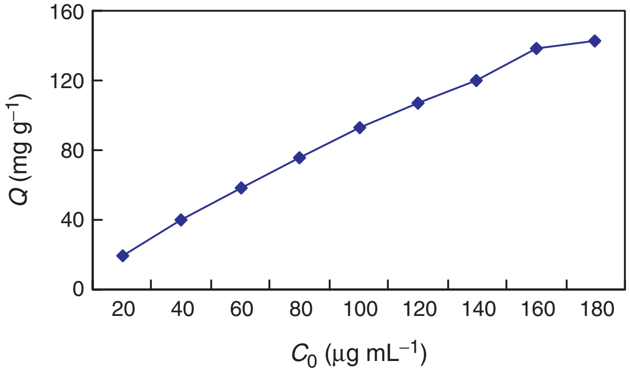


Figure 3. Effect of Pb(II) initial concentration on the adsorption quantity of Pb(II)-imprinted IPN. Other conditions: 100 mg of Pb(II)-imprinted IPN, 100 mL of Pb(II) solution, pH 4.0, shaking time 12 h, temperature 25°C.

The adsorption capacity of the imprinted IPN gel increased almost linearly with the initial concentration of Pb(II) ions. The average maximum Pb(II) adsorption capacity of the imprinted IPN gel was 138.6 mg g^{-1}, which was more than other adsorbents [25–28].

3.5 *Effect of elution rate*

In order to be able to reuse the adsorbent, Pb(II) must be eluted from the adsorbent. Because the coordination interaction of chelated Pb(II) ions could be easily disrupted under strong acid conditions, elution of Pb(II) ions from the Pb(II)-imprinted IPN in the column was made by passing HNO_3 solution as a desorption reagent. Pb(II) ions were released from the lead templates into the desorption medium. The experimental conditions show that Pb(II) ions could be quantitatively eluted with 10 mL of 0.5 mol L^{-1} HNO_3 with $>97\%$ recovery.

The flow rate of the 0.5 mol L^{-1} HNO_3 solution through the imprinted IPN in the column is a very important parameter for the time controls of desorption and analysis. In this experiment, the 0.5 mol L^{-1} HNO_3 solutions were passed through the Pb(II)-imprinted IPN in the columns at a flow rate that could be controlled by the peristaltic pump. The flow rate was maintained at 0.5–4.0 mL min^{-1}.

The results (figure 4) show that Pb(II) ions can be quantitatively eluted at flow rates below 1.0 mL min^{-1}. Thus, the flow rate of 0.5 mL min^{-1} which represents a better effect on desorption of Pb(II), was selected for further study.

3.6 *Pb(II)-imprinted IPN stability tests*

The repeated use of a commercial adsorbent is likely to be a key factor in industrial wastewater-treatment economics. Thus, the adsorption–desorption cycle was repeated 20 times by using the same imprinted IPN in order to demonstrate the reusability and stability of the Pb(II)-imprinted IPN. The results clearly showed that the IPN can be used repeatedly without losing their adsorption capacities. Therefore, the

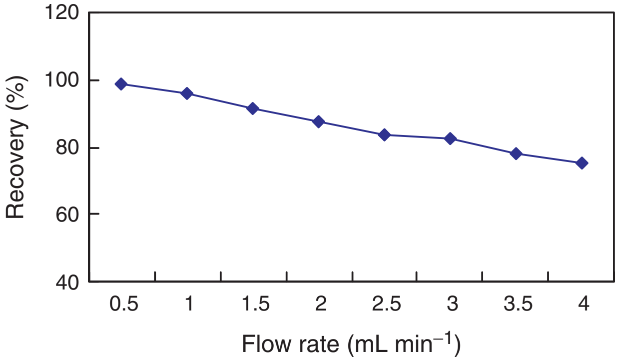


Figure 4. Effect of flow rate (mL min^{-1}) of elution reagent on recovery. Other conditions: 100 mg of imprinted IPN loaded Pb(II) ions, 10 mL of 0.5 mol L^{-1} HNO_3 solution, temperature 25°C.

Pb(II)-imprinted IPN shows a better reusability and stability towards Pb(II) in the environmental Pb(II) removal. The good stability might be due to the chemical and physical stabilities of epoxy resin as a main component of the Pb(II)-imprinted IPN [29, 30].

3.7 *Accuracy and precision of the analytical method*

Under selected conditions, the recoveries of 20 ng mL^{-1} Pb(II) ions in 100 mL solutions, enriched and determined simultaneously 11 times, are 95–100%. The precision of the method for a standard, evaluated as the relative standard deviation (R.S.D., $n = 11$), was 2.9%. The limit of detection (3σ), defined as the concentration of analyte giving signals equivalent to three times the standard deviation of the blank plus the net blank intensity for 100 mL of sample volume, was 0.3 ng mL^{-1}.

In order to determine the accuracy of the method, the proposed procedure has been applied to the analysis of lead in three standard reference materials (GBW 07403, soil; GBW 08619, water; GBW 07301, river sediment). The analytical results for the standard materials are in good agreement with the certified values. Moreover, the prepared imprinted IPN was applied for preconcentration and determination of Pb(II) in three natural samples collected from the environment. The samples were treated by the sample procedure above. Then, these solutions were introduced into the Pb(II)-imprinted IPN column system in the same way as described previously. The obtained results as well as the recovery tests listed in table 1 indicate the suitability of the present Pb(II)-imprinted IPN for preconcentration of Pb(II) from water and sediments.

4. Conclusion

The objective of this article was to investigate the characteristics of lead preconcentration of Pb(II)-imprinted IPN adsorbent synthesized by the metal ionic imprinted technique. The IPN of epoxy resin-triethylenetetramine and

Table 1. Preconcentration and determination of Pb(II) ions from three natural samples from Ningbo region, Zhejiang Province, P.R. China.

Sample	River sediment sample (μg g^{-1})	Soil sample (μg g^{-1})	Surface river sample (μg L^{-1})
Pb(II) found	4.643 ± 0.31	1.856 ± 0.16	5.257 ± 0.23
Recovery (%)	98.9	99.2	98.6
Error (%)	1.1	0.8	1.4

lead methacrylate-acrylamide-cross-linker was prepared by *in situ* sequential polymerization, and Pb(II)-imprinted adsorbent was obtained by removing Pb(II) ions from the IPN. The synthesis method of the Pb(II)-imprinted IPN is simple, rapid, and economic. The prepared ion-imprinted IPN adsorbent shows a high selectivity and adsorption capacity compared with other adsorbents. Moreover, it was applied to three natural samples and three standard reference materials with satisfactory results. The adsorbent shows a superior reusability and stability in practical applications and can be used several times without any considerable loss of adsorption capacity. Compared with previously used adsorbents, this ion-imprinted IPN clearly demonstrates better chemical and physical characteristics. To summarize, the Pb(II)-imprinted IPN gel is a suitable SPE adsorbent for lead adsorption from the water and sediment samples in the surrounding environment

Acknowledgements

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